

carbonate at an elevated temperature higher than 350°C. Consequently, it may be difficult to secure a constant performance in the treatment of the exhaust gas from such a vehicle engine of which the operation conditions are drastically fluctuated. Further, the removal of the nitrogen oxides by absorption is poor in the presence of carbon dioxide. Further more, in particular, a problem remains in the initial cleaning of the exhaust gas from the start of the operation until the temperature of the exhaust gas treatment apparatus reaches the high actuation level.

The carbon-containing particles in the exhaust gas can be effectively removed by capturing them with a filter which is often blocked with the carbon-containing particles and required to be frequently exchanged with a fresh one. The oxidative removal of the carbon-containing particles accumulated on the filter has been tried in the presence of a catalyst supported on the filter, the filter is often damaged by the steep temperature rise.

In a proposal, the carbon-containing particles in the exhaust gas are used to remove the nitrogen oxides and both of them are expected to remove simultaneously. But, a solid catalyst is used in the process and the solid carbon-containing particles can not be satisfactory captured and reacted, and the decrease in the nitrogen oxides is insufficient, too.

DISCLOSURE OF THE INVENTION

An object of the invention is to provide a method and an apparatus treating an exhaust gas by removing at least one of pollutants of carbon-containing particles and nitrogen oxides in the exhaust gas without consumption of materials which have economical or environmental problems, in no need of any complicated controlling mechanism and at a relatively low temperature. Further, another object of the invention is to provide a vehicle equipped with the apparatus.

In the invention, the carbon-containing particle means generally particulate, smoke (SM), soot, carbon, particle. Its component comprises solid carbon, unburned fuel, lubricating oil, sulfates combined water and the like.

Nitrogen oxides comprise mainly nitrogen monoxide NO and nitrogen dioxide NO₂ and may include small amounts of N₂O and N₂O₃ in the exhaust gas.

The conventionally proposed methods for simultaneously removing nitrogen oxides and carbon-containing particles by reducing the nitrogen oxides with the carbon-containing particles are not always effective, because the exhaust gas

carrying out the invention.

Fig.7 is a cross sectional plan view of another reaction zone device for carrying out the invention.

Fig.8 is a plan view of combination a reaction zone device and an after-treating device for carrying out the invention.

DESCRIPTION OF A PREFERRED EMBODIMENT

The liquid-including substance in the invention has at least partially liquid surface and can adhere to capture carbon-containing particles in the conditions of the invention. The substance includes liquid or a mixture comprising liquid and solid. The solid may be in any shape, for example, lump, particle or powder, but particle or powder is preferable. The mixture of liquid and solid may be fluid as in a suspension or not, but preferably has fluidity. Any proportion of solid to liquid in the mixture may be allowed as long as the mixture is adhesive. The content of the solid in the suspension is generally lower than 50 vol%, usually lower than 40 vol%, but it depends on the size and the shape of the solid particles.

un
qv
ed

The active component included in the liquid-including substance, which reacts with the carbon included in the carbon-containing particles to be converted to CO_2 and/or the salts including carbonic acid radicals, comprises salt including oxygen acid radicals of nitrogen. The oxygen acid radical of nitrogen comprises generally nitrite radical NO_2 and / or nitrate radical NO_3 , preferably nitrate radical. The salt including oxygen acid radicals of nitrogen is also produced by reaction of nitrogen oxides with the salt including carbonic acid radical under the operation condition of the system, if necessary, in the presence of free oxygen in the exhaust gas. The substance has at least one of nitrite radical and nitrate radical, and may include other anion radical harmless to the process in the invention, for example, basic salts having hydroxy radical, polynuclear salts having oxo bridges and salts having less the carbonate radical than the oxygen acid radical of nitrogen and the like. Similarly, the salt including carbonic acid radical also have the carbonate radical CO_3 and may contain other anions harmless to the process in the invention, for example, basic salts having hydroxy radical, polynuclear salts having oxo bridges and salts having less oxygen acid of nitrogen than the carbonate radical and the like.

qv

The salt including carbonic acid radical has generally a higher melting point and a lower solubility than the salt including oxygen acid radical of

For example, the saturated solution of magnesium nitrate have about 14% water by weight at a temperature of 200°C.

Some liquid substances harmless to the operation under the conditions in this invention may be used as a solvent medium, for example, oxygen acids of phosphorus or its salts, salts of bisulfuric acid and salts of pyrosulfuric acid and so on. For specific examples, orthophosphoric acid, metaphosphoric acid, polyphosphoric acid, potassium dihydrogen orthophosphate (KH_2PO_4), sodium bisulfate and potassium bisulfate etc. can be cited. Any amount of these solvents may be used, if the objects of the invention can be achieved.

Any concentration of the salt including oxygen acid radical of nitrogen in the total salts may be allowed in the liquid, if the objects of the invention are achieved, but it is generally more than 5%, preferably more than 20%, especially more than 50% by on a weight basis.

Catalysts are effective for operating the reaction zone smoothly in the invention, and metals with variable valences or noble metals and their compounds are used as the catalyst. Elementary metals, their compounds and mixtures of copper, vanadium, cobalt, nickel, molybdenum, cerium, silver, iron, manganese, lead and so on, and platinum noble metals group, such as platinum, palladium, rhodium, ruthenium, and iridium can be cited. These catalysts may be dissolved or dispersed in suspension in the liquid or carried on solid carriers and wetted with said liquid-including substance.

Further, the packings in the capturing zone of the reaction zone device may be constituted from these catalytic substance itself or the catalytic substance may be carried on the packings. When the catalyst is used in the form of solution, dispersion or suspension, the amount of the catalyst is not particularly limited, but in general, it is 0.001~20wt%, preferably 0.1~10wt% based on the liquid-containing substance.

Any amount of the liquid-containing substance in the reaction zone may be used, if the object of the invention can be achieved, but it varies depending on the desired levels of the removing rate of the pollutants and the desired duration time while the exhaust gas can be treated. In the case of an internal combustion engine, the amount is generally more than 0.1 liter, preferably more than 0.2 liter, and there is no upper limit, but it is generally less than 20 liter preferably less than 10 liter per 1 liter of a exhaust capacity in an internal combustion engine.

Any operating temperature in the reaction zone may be allowed, if the object

balls, cylinders, rings, saddles, bells, fiber, mesh, wire-mesh, Raschig rings, foams, monolith honeycomb and so on, and in these packings, mesh, fiber, wire-mesh, foam, monolith honeycomb are most preferable, because of their small pressure drop in spite of the large specific surfaces. They are generally made of metals, ceramics or heat resistant polymers.

The construction material for the reaction zone device is required to have high durability in the operation conditions, and is generally metals, ceramics or heat resistant polymers. The metals are, for example, iron, copper, nickel, chromium, molybdenum, titanium etc and their alloys, such as stainless steel, Monel, Inconel, Hastelloy A, B, C, D, F, and the ceramics are silica, alumina, magnesia, zirconia, silicon carbide, silicon nitride, cordierite, spodumene and so on. The heat resistant polymers are, for example, perfluorocarbon polymers such as polyperfluoroalkylene, polyperfluoroalkylenoxide, and silicone polymers etc.

The reaction zone may be made up at least one step in series or parallels, and if necessary, after treating device may be connected after the reaction device. The function of the after treating device is to treat the remains of the mist and/or pollutants from the reaction zone. For example, the same structure of said reaction zone device may be used as the after treating device with or without water as a capturing medium, and/or a capturing zone with solid carbon like char coal, coke and/or active carbon, if necessary, in the presence of known catalyst promoting the reaction of nitrogen oxides with the carbon, for example, alkali metals like potassium, copper, cerium, vanadium, molybdenum, etc and their compounds. As another example, the NO_x storage-reduction three way catalyst system may be used for treating the remaining nitrogen oxides.

er
9K
The composition of Nitrogen oxides in the exhaust gas varies depending on the condition of the source, but generally, the nitrogen oxides in the exhaust gas mainly consist of nitrogen monoxide NO which is hardly absorbed by the liquid-including substance, and on the contrary, nitrogen dioxide NO_2 can be easily absorbed with the liquid-including substance. Thus the nitrogen oxides entering into the reaction zone are preferable to be rich in nitrogen dioxide. The conversion of NO to NO_2 is preferably done by oxidation with oxygen remaining in the exhaust gas or air from outside in the presence of suitable oxidation catalyst. Said oxidation catalyst, if possible, can be substituted with the catalyst used in the reaction zone instead of said oxidation catalyst.

Solid catalysts carried with suitable carriers are used as said oxidation catalyst, and some of them are, for example, platinum, palladium, rhodium, ruthenium,

iridium, rhenium, silver, copper, ceria(CeO_2), manganese oxides, BaO-CuO binary oxide, lanthan-cobalt perovskite (LaCoO_3), vanadium pentaoxides, and their mixtures or mixed compounds etc, which carried on known carriers such as, for example, alumina, silica, titania, zirconia, magnesia, silica-alumina, cordierite, spodumene, silicon-carbide, or heat resistant alloys such as stainless steel or iron-chromium alloys etc. The carriers may be used in known shapes such as beads, cylinders, rings, saddles, bells, Rasich rings, monolith-honeycomb etc, but they are generally beads or preferably monolith-honeycomb of "flow-thru" structures for preventing the carbon-containing particles from accumulating and blocking in the packings.

The oxidation of nitrogen monoxide with oxygen over the oxidation catalyst is carried out generally in a temperature range of from 100°C to 500°C , in particular, from 200°C to 450°C .

In the case where the exhaust gas to be charged into the oxidation reactor has a low temperature, it can be heated with a usual heating means, for example, an electric heater or other heat sources such as combustion gas, or by adjustment of the operation conditions of the exhaust gas sources, for example, by throttling the internal combustion engine. (Cf. S. A. E. Report No. 830085 (1983)).

In the present invention, the carbon-containing particles, carbon monoxide, hydrocarbons and the like as reducing substances in the exhaust gas directly or indirectly react with nitrogen oxides, oxygen and the like whereby these substances in the exhaust gas is converted to carbon dioxide, nitrogen and water. Accordingly, in order to decrease the emission of these reducing substances and nitrogen oxides outside the system to the level lower than the allowable limit, these reducing substances are desirably balanced stoichiometrically with the nitrogen oxides.

In the case where the reducing substances are underbalanced for a long time the substances capable of absorbing the nitrogen oxides, for example, the salts including carbonate radical or the like in the liquid-including substance fall into shortage to insufficiently eliminate the nitrogen oxides and the object of clean up of the exhaust gas can not be attained, because the remaining nitrogen oxides are finally emitted out of the system.

In the meantime, the shortage of the nitrogen oxides causes the lack of the salts including oxygen acid radical of nitrogen in the liquid-including substances, and the carbon-containing particles and other reducing substances are finally emitted out of the system, as they are not sufficiently removed.

Thus, the stoichiometric ratio of the reducing substances including the carbon-containing particles to the nitrogen oxides determines the quality of the exhaust gas emitted out of the system and is required to be kept optimal.

As a method for controlling the ratio of the carbon-containing particles to the nitrogen oxides in the exhaust gas flowing in the device according to the present invention, can be cited, for example, exhaust gas recirculation (E. G. R.), change in fuel injection pressure, adjustment of fuel injection time and the like. In case of the shortage of the reducing substance including the carbon-containing particles and the like, reducing substances, for example, hydrocarbons as methane, liquefied petroleum gases (L. P. G.), fuel oil or the like, alcohols as methanol, ethanol or the like, hydrogen, carbon monoxide may be added from the outside of the system to the exhaust gas to be charged into the reaction zone having the liquid-including substance. In another case, carbon particles produced by catalytic reaction or incomplete combustion of fuels may be charged.

In addition, in order to remove the remaining nitrogen oxides, the after-treating device with solid carbon or the NO_x storage-reduction three way catalyst system may be applied.

It has been known that the effective life time of known means for treating of the exhaust gas is remarkably influenced by the impurities included in the fuel, for example, sulfur. In the exhaust gas treatment for diesel engine, wherein fuel of high sulfur content is often used, the catalyst supported on solid carriers used in the known means can not yet attain the practical catalyst life.

On the contrary, the liquid-including substance according to the present invention, differing from the catalysts carried on solid carriers that are restricted in their catalyst contents, can still retain the ability for a long term to treat the nitrogen oxides and the carbon-containing particles by fitting a large capacity of the reaction zone device, even after a large volume of the exhaust gas is treated to absorb SO_x.

In addition, even when the ability to treat the exhaust gas in the liquid-including substance have dropped after its long operation, the ability can be recovered easily and inexpensively by draining a part or all of the old contents, then introducing freshly prepared the liquid-including substance or the compositions which can be form the substance.

When the solid carrier-supported catalyst such as the NO_x absorption reduction type three way catalyst system is set to the downstream of the reaction zone of this invention in order to remove nitrogen oxides, a long